

## **Interaction between the Pozzolanic Reaction of Fly Ash and the Hydration of Cement.**

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### Abstract

The hydration of fly ash - cement binders includes two interrelated processes : the hydration of cement clinker and the pozzolanic reaction of fly ash. Free lime is released during the hydration of cement clinker and activates the pozzolanic reaction of fly ash, where it will be absorbed. In this study four paste mixtures with a fly ash-to-cementitious material ratio ranging from 0.00 to 0.67 and a constant water content have been subjected to isothermal calorimetry. A third hydration peak is noticed for the pastes with fly ash. The peak increases with increasing fly ash content. At different ages, thermogravimetric and differential thermal analyses have been performed on the mixtures. During the third hydration peak, the free lime content of the binders with fly ash increased relatively more than of the binder with ordinary portland cement. The start of the pozzolanic reaction was assumed at the moment when the free lime content decreased. The latter reaction seemed to start earlier with increasing fly ash content.

### 1. Introduction

It is well-known that the hydration of fly ash – cement binders includes two complex phenomena : the hydration of cement clinker and the pozzolanic reaction between fly ash and free lime. Researchers have pointed out in the past that both processes accelerate each other [1,2]. The active effect of fly ash in a fly ash-cement binder can be divided into two aspects: the pozzolanic activity of fly ash and its ability to promote the hydration of cement [1]. The most difficult part is separating the kinetics of both processes in order to determine the individual hydration degree of the cement clinker and the pozzolanic reaction degree of fly ash [1,2]. The hydration of cement is a much faster process than the pozzolanic reaction of fly ash, which can be still active, even after one year. Several researchers tried to distinguish the contributions of cement and fly ash in

the overall hydration reaction, all with their own measuring techniques [1,2]. Wang reported an increase of the hydration degree of cement and a decrease of the pozzolanic degree of fly ash for binders with increasing fly ash content and constant water to binder ratio [1]. It still remains difficult to assess from the measured results when the start of the pozzolanic reaction occurs and when the hydration of the cement clinker reaches an ultimate value. Two techniques often used are isothermal calorimetry and thermal analysis (TGA/DTA). Both techniques produce results which are dependent on each other, as mentioned by Pane et al [2]. When only one of these two techniques is performed, it is difficult to assess from the measurements whether the measured effects are caused by the pozzolanic reaction of fly ash or its promoting role in the hydration of the cement clinker. Conclusions often depend on the interpretation of the start of the pozzolanic reaction. In this study, tests results from thermogravimetric experiments and isothermal hydration tests are first analyzed by assuming that the fly ash only promotes the cement hydration. The start of the pozzolanic reaction of the fly ash is considered to be at the time when the free lime content of the binder starts to decrease.

## 2. Materials and experimental program

### 2.1. Materials

An ordinary portland cement (CEM I 52.5 N), complying with the European Standard EN 197-1 (2000) was used in all mixtures. In this study the detailed effect of a fly ash, Class F according to ASTM Standards and with a low calcium oxide content according to EN 450, was studied on the hydration process of a portland cement–fly ash binder. Table 1 lists the chemical compositions of the portland cement and fly ash according to the EN 196-2, together with the free CaO of the fly ash, determined in accordance with NBN EN 450-1. The theoretical mineralogical composition of the clinker, derived from the chemical analysis using the Bogue calculation, is also given in table 1 for portland cement.

### 2.2. Experimental set-up

Table 2 summarizes the mixture proportions of the four investigated binder pastes. The water to cementitious materials ratio was kept constant at 0.40.

Immediately after mixing, 14 grams of each binder paste were placed in a calorimeter to measure isothermally the exothermal hydration process. This test was performed for each binder mixture three times for two different isothermal conditions: 20°C and 35°C. The heat evolved per time unit was monitored and recorded at 20-seconds intervals.

Table 1 : Chemical analysis and loss of ignition (LOI) of the studied cement and fly ash

|                                    | CEM I 52,5 N | Fly ash |
|------------------------------------|--------------|---------|
| SiO <sub>2</sub> (%)               | 19.6         | 51.3    |
| Al <sub>2</sub> O <sub>3</sub> (%) | 4.9          | 4.0     |
| CaO (%)                            | 63.6         | 3.5     |
| Fe <sub>2</sub> O <sub>3</sub> (%) | 3.1          | 1.3     |
| MgO (%)                            | 0.9          | 1.9     |
| SO <sub>3</sub> (%)                | 3.3          | 0.9     |
| LOI (%)                            | 2.1          | 4.0     |
| Free CaO (%)                       | -            | 0.02    |
| C <sub>3</sub> S (%)               | 63.4         | -       |
| C <sub>2</sub> S (%)               | 8.4          | -       |
| C <sub>3</sub> A (%)               | 7.4          | -       |
| C <sub>4</sub> AF (%)              | 10.0         | -       |

Table 2 : Mixtures portions of the studied binder pastes

| Mixture   | C/CM (-) | FA/CM (-) | W/CM (-) | W/C (-) |
|-----------|----------|-----------|----------|---------|
| Reference | 1.00     | 0.00      | 0.40     | 0.40    |
| FA35W40   | 0.65     | 0.35      | 0.40     | 0.67    |
| FA50W40   | 0.50     | 0.50      | 0.40     | 0.80    |
| FA67W40   | 0.33     | 0.67      | 0.40     | 1.21    |

The hydration kinetics were also studied using TGA and DTA. The ages of testing were 3, 12, 18, 24, 48, 72 hours and 7, 14, 28, 56, 120 days (respectively 168, 336, 672, 1344, 2880 hours). The samples are made according to [2]. For each binder mixture, cylinders with 74 mm height and 48 mm diameter were made. The cylinders were rotated at a speed of 5 rotations per minute for a period of six hours to prevent bleeding. Afterwards they are cured in a water bath at a temperature of 20 ± 2°C. At the desired age of testing, the cylinders were ground into small pieces and soaked in dry methanol to avoid further hydration. According to [3] methanol reacts with Ca(OH)<sub>2</sub> forming Ca(OCH<sub>3</sub>)<sub>2</sub>, methylated complexes or carbonate-like products. This is however not accepted by all investigators [4]. To minimize possible carbonation by atmospheric CO<sub>2</sub>, the specimens, soaked in methanol, were kept in sealed, small containers.

After one week, the samples were placed in a dessicator to remove the methanol. All specimens were decomposed at a temperature range from 25°C to 1100°C at a rate of 10°C/min. This test procedure is also given by Pane et al. [2]. For the paste binder FA50W40 a comprisal study was made of the thermogravimetric weight loss at the age of one day between samples immediately tested and samples first soaked in methanol for a week. No significant differences between both test results could be noticed.

### 3. Experimental results and discussion

#### 3.1. Isothermal hydration test

Immediately after mixing a first peak appears. Because the mixing takes place outside the calorimeter, this peak has not been measured entirely. In practice, concrete is not cast immediately after water addition : the heat corresponding to the first peak remains in the concrete mixer and only contributes to a slightly higher initial temperature [5,6,7]. The heat generation during the first peak only amounts to a few percent of the total heat liberated. The first peak can be left out from the further analysis [5,6]. The second correction performed on the measured data is due to the bias of the calorimeter [8]. The magnitude of the bias can be modelled by a uniform distribution with an average of 0,07 Joule per gram solid material and per hour.

With the corrected rate of heat development, the cumulative heat generation  $Q$  is calculated. When the rate of heat development as well as the cumulative heat is normalized by the weight of the cement of each binder, then all measured heat is considered to be derived from the hydration of cement and all water is considered to be available for the latter reaction. The active effect of fly ash in this case is limited to its promoting role in the hydration of cement clinker. The maximum, theoretical heat release of each binder mixture can be calculated by adding the enthalpy (of complete hydration) of each cement mineral [9,10,11]. Table 3 lists the measured and the calculated, cumulative heat development  $Q_{\text{experiment}}$  and  $Q_{\text{Bogue}}$ . Both parameters are expressed as Joule per gram cement and per hour. It should be noted that  $Q_{\text{experiment}}$  is the total, cumulative heat production at 7 days. Only the total heat production of the reference binder at 35°C has reached an asymptotic, final value. The total heat release of the other binders is still slightly increasing after 7 days. This increase is higher for the binder with higher fly ash content, which could indicate that the pozzolanic reaction is active at this moment (7 days). The measured signal of the heat released during

this latter reaction, will however be too small to be representative for a quantitative estimation of the pozzolanic reaction.

The ratio of  $Q_{\text{experiment}}$  to  $Q_{\text{Bogue}}$  is a measure for the ultimate hydration degree of the cement. Mill formulated an ultimate hydration degree based on the water-to-cement ratio [12].

$$\alpha_{\text{Mill}} = \frac{1.031 \frac{W}{C}}{0.194 + \frac{W}{C}} \quad (\text{equation 1})$$

In table 3 and equation 1 the ultimate hydration degree of Mill is mentioned as  $\alpha_{\text{Mill}}$ . This ultimate hydration degree is for all binders much smaller than the experimental hydration degree  $\alpha_{\text{experimental}}$  at 35°C. The FA50W40 and FA67W40 binders reach at seven days a hydration degree of 0.99 and 1.11 respectively, which is physically impossible. This indicates that a part of the heat release is caused by the pozzolanic reaction which has already started before 7 days in those mixtures.

Table 3 : Total heat at 7 days, as the average of three measurements and corresponding degree of hydration

|               |                                  | Reference | FA35W40 | FA50W40 | FA67W40 |
|---------------|----------------------------------|-----------|---------|---------|---------|
| 35°C          | $Q_{\text{experiment}}$ (J/g)    | 340       | 403     | 441     | 494     |
|               | $\alpha_{\text{experiment}}$ (-) | 0,76      | 0,90    | 0,99    | 1,11    |
| 20°C          | $Q_{\text{experiment}}$ (J/g)    | 315       | 343     | 371     | 376     |
|               | $\alpha_{\text{experiment}}$ (-) | 0,71      | 0,77    | 0,83    | 0,84    |
| Theoretically | $Q_{\text{Bogue}}$ (J/g)         | 447       | 447     | 447     | 447     |
|               | $\alpha_{\text{Mill}}$ (-)       | 0,69      | 0,78    | 0,83    | 0,89    |

Figures 1 and 2 give the average development of both parameters in time for all binders at 20°C and at 35°C respectively. The second peak tends to decrease with increasing fly ash content as well at 20°C, as at 35°C. The acceleration period in the rate of heat development at 20°C and 35°C seems somewhat slower for the binders with fly ash. This effect becomes more noticeable with increasing fly ash content and is probably caused by a dispersion effect. This latter effect is due to the larger water availability for the cement hydration. This effect can however not be very important, since the hydration is at that time not yet diffusion-controlled. This is also noticeable in the cumulative heat development at 20°C and 35°C : the difference between the different binders is very small during the induction period. The effect of the larger water availability for the hydration of the cement, becomes more noticeable after 24 hours : the cumulative heat increases with increasing fly ash content (and with increasing water to cement ratio). The larger water to cement ratio of the binders with fly ash

is the main reason for the larger, cumulative heat at 7 days of the binders with fly ash. By multiplying the ultimate hydration ratio of Mill with the theoretical heat release according to Bogue, the heat release of the cement hydration of the FA35W40, of the FA50W40 and of the FA67W40 binders should be 310 J/g, 350 J/g, 371 J/g and 397J/g respectively. The measured heat at 35°C of these binders amounts 403 J/g, 441 J/g and 494 J/g. The difference between the measured and theoretical heat is more or less proportional to fly ash content of the binders. The difference can therefore be attributed to the pozzolanic reaction.

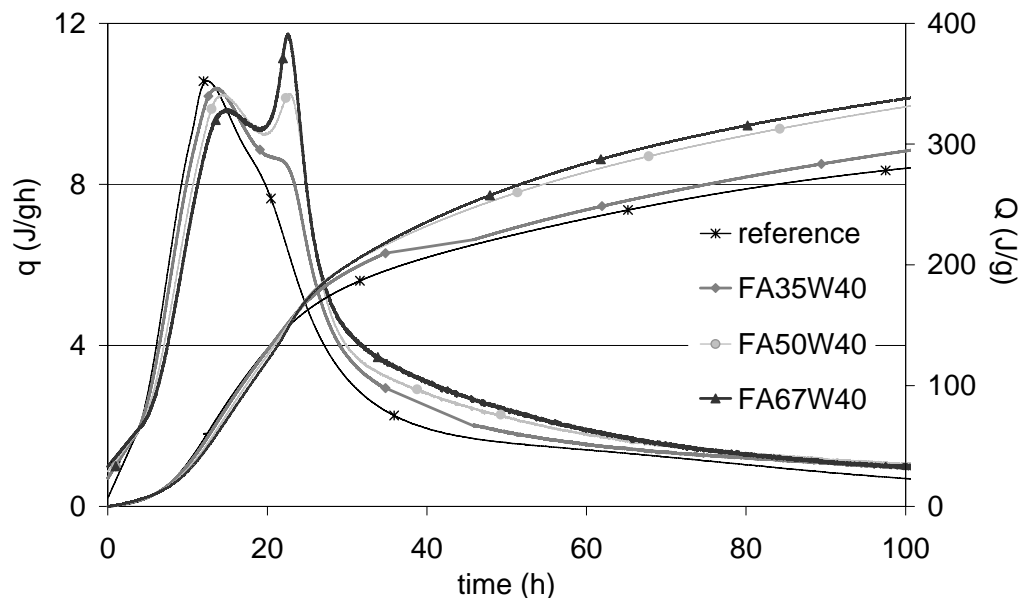


Figure 1 : Average rate of heat development  $q$  (Joule per gram cement) and total cumulative heat (Joule per gram cement) of three measurements at 20°C

At 20°C and at 35°C a third hydration peak appears at 24 hours, respectively 16 hours. This peak increases with increasing fly ash content of the binder. The time shift between the third and second peak in the heat evolution at 35°C is not so clear noticeable as it is at 20°C. The small appearance of a third peak in the heat development of the reference paste can probably be correlated with the hydration of  $C_3A$  (the reaction of ettringite to monosulphate [8]). The  $C_3A$  content of the cement used in this study is around 7,4%, which is low to be the only reason for the third hydration peak of the fly ash- cement binders. A possible other reason can be found with the fly ash: either the fly ash promotes the hydration of the cement and serves as nucleation site for the cement hydration (and more specific to the hydration of  $C_3A$ ) or the fly ash is not inert : the pozzolanic reaction could manifest itself in the third hydration peak. The latter theory is in contradiction to some published data, which report that the pozzolanic

reaction starts at 7 days or even at 28 days (at a curing temperature of 20°C).

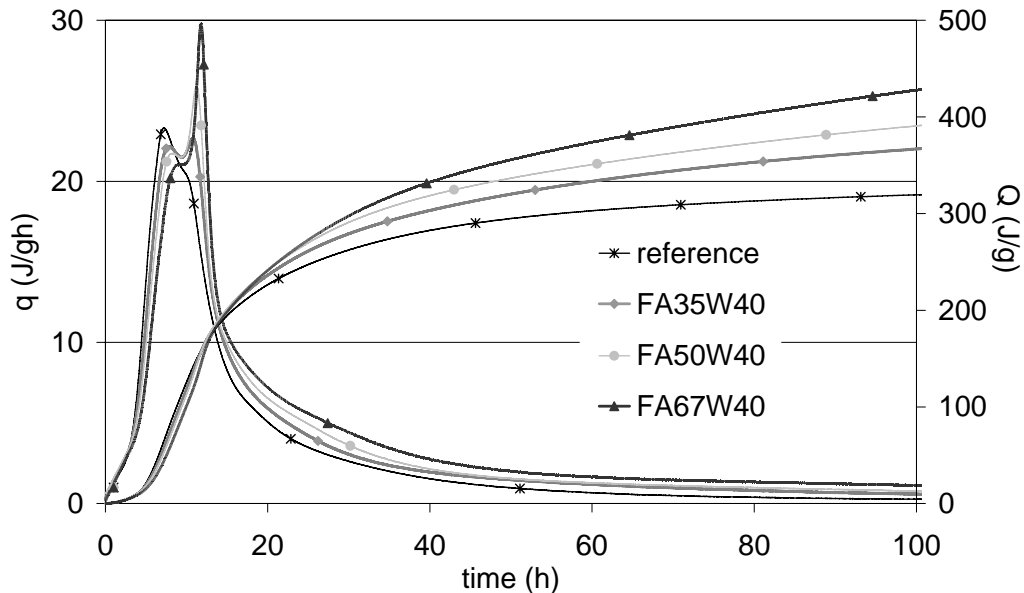


Figure 2 : Average rate of heat development  $q$  (Joule per gram cement) and total cumulative heat  $Q$  (Joule per gram cement) of three measurements at 35°C

It can however be a combined action of both phenomena. According to Uchikawa [13], on contact with water, the surfaces of fly ash grains are protonically attacked by  $H_3O^+$ , formed by the dissociation of water. It brings gradual dissolution of  $Na^+$  and  $K^+$  and results in a Si and Al rich amorphous layer on the surfaces. Dissolved  $Na^+$  and  $K^+$  accelerate the dissociation of water, intensify the protonic attack of water and accelerate the dissolution of  $SiO_4^{4-}$  and  $AlO_2^-$ , which combine with  $Ca^{2+}$  and increase the thickness of the layer. The negatively charged grains from fly ash also absorb  $Ca^{2+}$ , formed by the hydration of  $C_3A$ ,  $CaSO_4 \cdot H_2O$  and  $Ca(OH)_2$ , on their surface. By the adsorption of  $Ca^{2+}$  in liquid phase and by presenting the site of precipitation of ettringite, fly ash could accelerate the hydration of  $C_3A$  and the time of conversion of hexagonal Ca-Al hydrate to cubic  $C_3AH_6$ .

By transforming the time axis to an axis of reaction degree, defined by equation 1, and by normalizing the rate of heat development  $q$  of portland cement with its maximum value of the second peak, the normalized curves  $q/q_{max}$  seem to have the same shape and same location of the second and third peak, independent from the temperature. This has been pointed out by several researchers [5-7]. This normalization has also been performed in this study for the binder mixtures with fly ash (figure 3). The curves in

figure 3 have been normalized by the second peak of the rate of heat development  $q_{\max 2}$ . The total heat release at 35°C is taken as  $Q_{\max}$  for each binder mixture. In figure 3 the shape of the curves of the binders with fly ash seems to be independent from the temperature, but the location of the third peak varies somewhat with the temperature : at 35°C the third peak of fly ash – cement binders occurs at smaller reaction degrees compared to the measured third peak at 20°C. This dependency, however becomes smaller with increasing fly ash content.

$$r = \frac{Q(t)}{Q_{\max}} = \frac{1}{Q_{\max}} \int_0^t q(t) dt \quad (\text{equation 2})$$

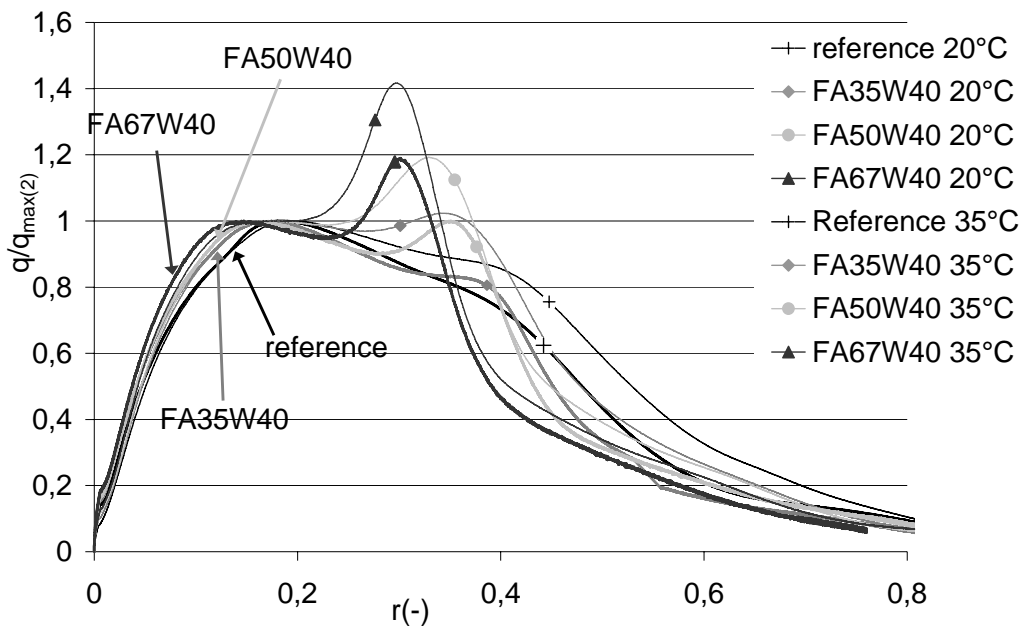


Figure 3 : normalized average rate of heat development  $q/q_{\max 2}$  (-)

### 3.2. Thermal analysis

Differential and thermogravimetric analysis were performed on the binder pastes at different ages. The data from the differential analysis were used to assess the boundaries within which the material decomposed. The results from the thermogravimetric analyses were studied to determine the amount of chemically bound water  $w_b$  (non-evaporable water), defined as the mass loss between 105°C and 1100°C, the amount of free lime and the amount of calcium carbonate.

On the calculation of the bound water  $w_b$  three corrections were made. The mass losses corresponding with decomposition of the free lime and the calcium carbonate and the mass loss of the unreacted binder paste



were subtracted from the mass loss within the temperature range of 105 – 1100°C. The mass loss of unreacted cement material was 0.009 gram per gram cement. The weight loss corresponding to the loss of calcium carbonate and free lime was not corrected, since a correction does not bring a significant change to the overall analysis, as mentioned by Pane and Midgley [3,9].

Figure 4 gives the free lime content versus the measured weight losses  $w_b$ , corresponding to the amount of bound water available in the mixtures reference, FA35W40, FA50W40 and FA67W40. The weight loss  $w_b$  has been normalized by the cement content. The free lime was calculated from the measured, thermogravimetric loss between 410°C and 500°C and has also been normalized by the cement content. The variation coefficient of the  $w_b$  and of free lime content of FA50W40 at the age of one day is 0,12% resp. 0,22%. The measured thermogravimetric loss between 600°C and 750°C, corresponding with the decomposition of calcium carbonate into carbon dioxide and calcium oxide, is also shown in figure 4 (dotted line). The latter parameter is expressed as percentage of the ignited sample weight and has been reduced with the initial loss between 600°C and 750°C of the unreacted binder material.

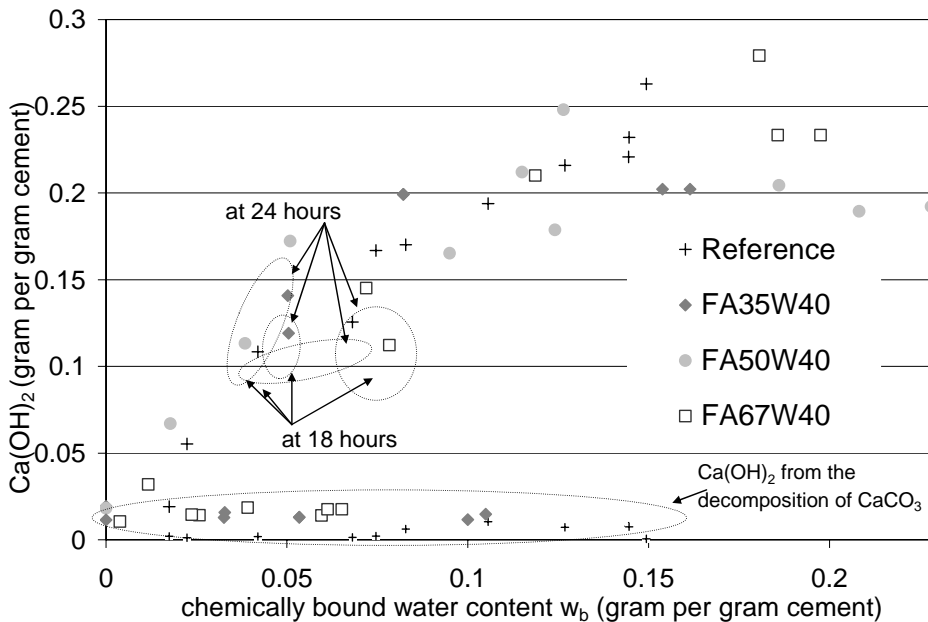


Figure 4 : Development of free lime and evolution of measured carbon dioxide loss versus the measured chemically bound water

By comparing the evolution of the chemically bound water (per gram cement) of the binders reference and FA50W40 with time, it can be seen

that the amount of chemically bound water increases more after 28 days for the binder with fly ash than for the binder with only portland cement. This reaction is due to the pozzolanic activity of the fly ash. Measurements of the binders FA35W40 and FA67W40 after 28 days are currently not yet available.

The evolution of the measured calcium hydroxide content is an indication for the start of the pozzolanic reaction : the reaction of the fly ash manifests itself when the free lime content of the binder with fly ash remains more or less constant or starts to decrease. Figure 5 gives the measured free lime content per gram cement at different ages. The free lime content of the reference binder with only portland cement increases with time, while the calcium hydroxide content of the binders with fly ash increases up to a certain time and remains constant (FA35W40) or starts to decrease afterwards (FA50W40). This decrease can be explained by the fact that free lime is consumed during the pozzolanic reaction. From 2 days on, the free lime content of the FA35W40 binder stays constant. From 7 days on, the free lime content of the FA50W40 binder starts to decrease. At 3 days, the measured calcium hydroxide content of the FA67W40 seems very high, compared to the reference binder. This value does not seem realistic and has not been taken into account in the further analysis.

Up to 18 hours the free lime content of the different mixtures do not differ significantly from each other. Between 24 hours and 3 days the free lime content of the binders with fly ash (except for the FA50W04 at 2 days) is higher than for the reference paste. This can also be explained by the larger water to cement ratio of the binders with fly ash. The lower calcium hydroxide content of the FA35W40 and FA50W40 at 14 days, compared to the free lime content of the reference binder, is due to the pozzolanic reaction.

The previous observations do not explain the appearance of the third peak in the rate of heat development (Figs 1 to 3). In figure 4, the circles drawn in the figure, correspond with the evolution of free lime and chemically bound water during the third hydration peak. During this period the free lime content of binders with fly ash increases relatively faster than of the binder with only portland cement. The increase is most significant for the binder with 50% portland cement. The chemically bound water, however, does not seem to increase.

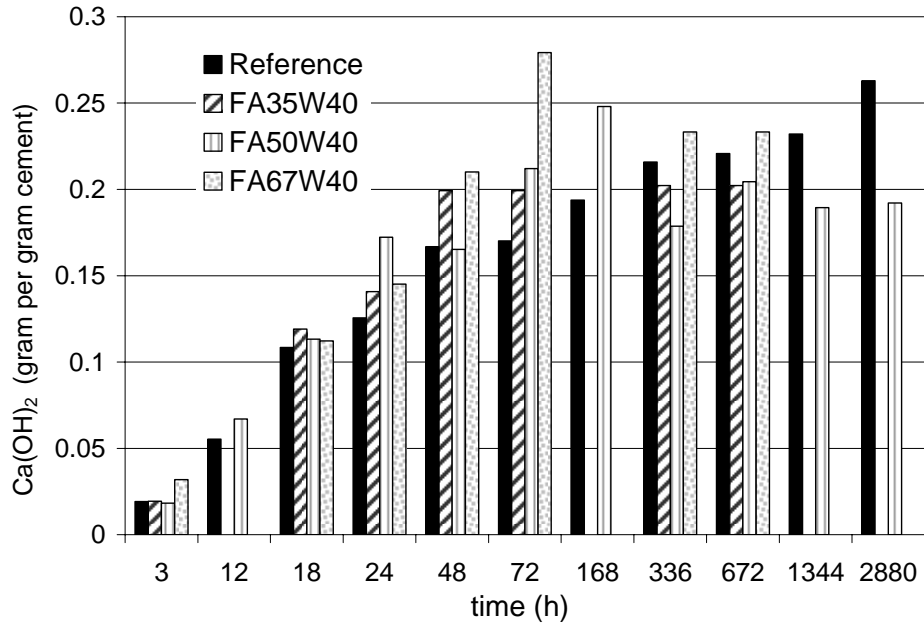


Figure 5 : Total calcium hydroxide content

#### 4. Conclusion

From the isothermal hydration tests and the thermogravimetric tests performed on binders with constant water content and a different fly ash to cementitious material ratio, the following conclusions can be drawn:

1. The total, cumulative heat at 7 days increases with increasing fly ash content. This increase is mainly due to the larger availability of water for the hydration of the cement. The experimental hydration degree of the cement at 7 days and at an environmental temperature of 35°C is larger than the ultimate hydration degree of Mill. The difference between the latter theoretical and the experimental value increases proportionally with the fly ash content.
2. A third hydration peak appears in the rate of heat development of the binders with fly ash. This peak increases with increasing fly ash content. At the same time of this peak, a relative larger increase of the calcium hydroxide was noticed for the binders with fly ash than for the binder with ordinary portland cement.
3. The calcium hydroxide content increases with time for the binder with ordinary portland cement and reaches a maximum at 3 to 7 days for the binders with fly ash. Afterwards the free lime remains constant or starts to decrease for the fly ash-cement binders, caused by the pozzolanic reaction of the fly ash.

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